3: Isotopic Analysis and Evolved Gases

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3.1. INTRODUCTION

Precise measurement of the chemical, elemental, and isotopic composition of surface material and gases, and observed variations in these compositions, can contribute significantly to our knowledge of the ultimate source(s), ages, and evolution of solar system material. This chapter deals with isotopic analysis and evolved gases. These analyses are mostly, but not exclusively, made by mass spectrometers or some other type of mass analyzer, and can address three broad areas of interest:

1. Atmospheric composition: isotopic, elemental, and molecular. Mass spectrometers have measured the atmospheres of most of the terrestrial planets, and are beginning to be applied to the outer planets and primitive objects (see Table 3.1).

These are the easiest measurements to make, since the material to be analyzed is already in the gas phase. Since the reconnaissance of the solar system's major atmospheres is nearly complete, the next generation of atmospheric mass spectrometers will have to be able to outperform previous experiments to be scientifically useful. Specific measurement goals are discussed below.

2. Gases evolved from solids. Usually, this involves releasing volatile elements from near-surface samples by heat-ing, acid dissolution, or other selective process, followed by mass analysis. Laser ablation extraction also produces a gas (actually, a plasma), but differs from other techniques in that it is more selective spatially (spot sizes in the 100-μm range) but less selective chemically (ionizing virtually every atom within a small volume). Lack of chemical sensitivity is a problem in isotopic analyses of trace constituents, but is an advantage in determining the abundances of various elements. Evolved gas analyzers have not been flown on any spacecraft, with the exception of the LIMA-D and DION experiments (*Sagdeev et al.*, 1986) on the ill-fated Phobos mission.

3. Solids. On many bodies, analyses of solids may have the greatest scientific payoff because radiometric dating of rocks (finding ages using the abundances of radioactive isotopes and their decay products) is the most precise and reliable way to determine quantitative planetary chronology. In addition, isotopic composition of nonradioactive isotopes can be diagnostic of the origin and evolution of planets. These analyses are the most difficult considered because the elements with the largest and most interesting isotopic variations are often rare, and isotopic shifts in the common elements are often subtle. The only successful analysis of solids *in situ* by a spacecraft was the PUMA analysis of dust from Comet P/Halley (*Jessberger and Kissel*, 1991). However, we have abundant and precise information on the isotopic composition of solids from Mars (in the form of martian meteorites; *McSween*, 1994) and the Moon (both lunar meteorites and the returned Apollo samples; *Warren*, 1994).

Current isotopic data on nine elements where information is available (mostly from *in situ* analysis, but also from meteorites and telescopic observations) are summarized in Fig. 3.1. This figure emphasizes the dynamic range required for meaningful isotopic studies—ratios of 10^2 or 10^3 are common, and He and H isotopes often have even larger abundance ratios. The figures also show that, for many elements, isotopic variations from one body to another are small—the size of the points on the plot corresponds to 5–10% uncertainties, comparable to the precision of most spacecraft measurements. However, isotopic variations are commonly even smaller. The extreme example is O, where studies of meteorites have shown that there is a tremendous amount of genetic information in the isotopic ratios, but only if they can be measured to 0.1% accuracy or better (*Clayton et al.*, 1991, and references therein).The next section of this chapter is a discussion of the scientific problems that could be addressed by evolved gas and isotopic analysis. This is followed by a discussion of the types of instruments that might be considered. Finally, there is a discussion of some specific technical problems that need to be solved to address some of the specific scientific questions.

TABLE 3.1. Missions on which mass spectrometers have been flown.

| Location/Mission	Type of Mass Spectrometer	Principal Constituents	Mission Status
Moon/Apollo 17	Single-focusing sector	Ar, Ne, H	Operated successfully for 10 lunations.
Mars/Viking			
Atmospheric	Mattauch-Herzog double-focusing sector	CO_2, N_2, Ar	Operated successfully on surface.
GC-MS	Nier-Johnson double-focusing sector		Operated successfully on surface.
Venus/Pioneer Venus			
Large probe	Single-focusing sector	CO_2, N_2, Ar	Operated successfully through entire atmosphere.
Bus	Mattauch-Herzog double-focusing sector		Operated successfully until loss of signal in upper atmosphere.
Comet			
P/Halley/Giotto	Nonstandard double-focusing energy analyzer	H_2O, CO, CO_2, NH_3, CH_4	Operated successfully until 1000 km from comet when spacecraft hit "wall" of dust.
Jupiter/Galileo	Quadrupole		In flight.
Saturn/Cassini	Time of flight		In preparation.
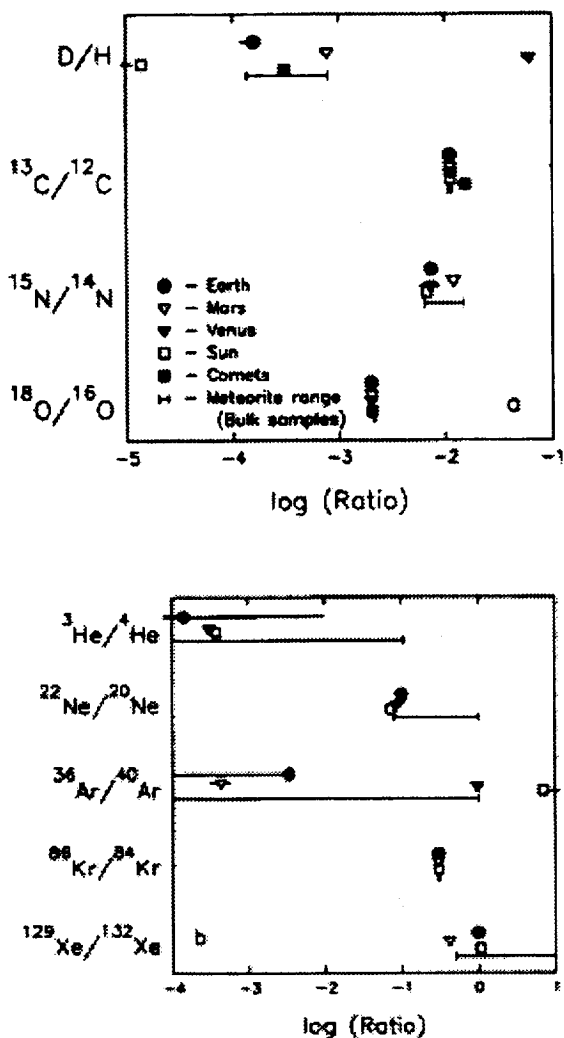
Fig. 3.1. Isotopic ratios of the major isotopes of (a) the reactive elements H, C, N, and O and (b) the noble gases. For Earth, the lines extending from the atmospheric point are the ranges observed in terrestrial rocks. Points with arrows are those where the ratio is off scale. Data from *Faure* (1986), *Epstein and Taylor* (1972), *Pepin and Carr* (1992), *Swindle* (1988), *Göbel et al.* (1978), *Eberhardt et al.* (1995), *Hoffman et al.* (1980), and *Schultz and Kruse* (1989).

We spend considerable effort on the question of whether any *in situ* technique can give a scientifically useful age of a rock. The usual assumption is that ages can only be determined on returned samples because the sample preparation and measurement precision needed are beyond the reach of spacecraft instruments (*Drake et al.*, 1987). This claim appears to be true with current instrumentation. However, we concur with *COMPLEX* (1994, p. 63) that "determination of even relatively imprecise ages can be very valuable in some cases. The flexibility, affordability, and feasibility of achieving many ... goals would be greatly enhanced by development of even crude dating techniques that could be placed aboard landed science packages."

3.2. SCIENCE ISSUES

In this section we briefly review the science questions that can be addressed by evolved gas and isotopic analysis. We rely heavily on *COMPLEX* (1994) for our selection of the important questions addressable by these techniques for each object. We will work our way through the solar system roughly in order of ease of access to objects.

3.2.1. Moon

Practically all elements and their isotopes have been measured in returned lunar samples (*Heiken et al.*, 1991). Volatile gas analysis of the lunar regolith materials returned by Apollo missions have revealed a unique isotopic composition for implanted solar wind gases and solar cosmic ray products compared to other objects in the solar system. How can *in situ* measurements improve the knowledge brought by these measurements? We discuss three specific questions, all of which are put in more context by *LExSWG* (1992).

Lunar water. The existence of lunar H_2O remains an issue of debate. The potential for the existence of water ice in permanently shadowed craters in lunar polar regions has long been argued (e.g., *Ingersoll et al.*, 1992, and references therein). If water ice is present in the polar regions, it could potentially be an important resource, as well as being scientifically interesting. In addition, it appears that under conditions at the lunar surface, solar H should reduce silicates to form H_2O, either through direct implantation or through mixing of regolith with hot gas generated in large meteorite impacts. In early D/H and $^{18}O/^{16}O$ studies of lunar soils, terrestrial contamination could not be ruled out. In fact, *Epstein and Taylor* (1972) concluded (from δD and $\delta^{18}O$ values) that the "lunar water" extracted from returned lunar samples was primarily of terrestrial origin, probably from the Apollo spacecraft and astronauts. To find water in the regolith would require that technology be found to assist in avoiding or eliminating terrestrial contamination by water in instruments landed at the lunar surface. To complement earlier laboratory determinations, *in situ* instrumentation must be capable of measuring with something approaching the 1% accuracy specified by *COMPLEX* (1994).

Characterization of the ancient solar wind. Since the Moon's surface may be regarded as a passive collector of solar radiation for most of its history, attempts to determine secular variations in solar activity by examining the record in regolith materials have long been a part of lunar sample studies (*Pepin et al.*, 1980). Correlations have been sought between isotopic measurements of gases, such as D/H and $^{4}He/^{3}He$, and other time-dependent parameters. These efforts have suffered from the inherent lack of precise knowledge of the regolith history of the examined samples. Most returned lunar samples, including cores of lunar regolith, do not testify to a well-defined lunar stratigraphy, which would be required for development of a relative timescale. Local stratification for the lunar regolith, which has preserved a true sequence of

meteoritic bombardment, may yet be discovered through robotic geology. Such a discovery followed by *in situ* measurements of solar wind elements and their isotopes may provide valuable information on early solar history. These measurements should be made with the same precision (a few percent or better) as previous laboratory measurements.

Characterization of the lunar atmosphere. Although the lunar atmosphere is extremely tenuous, its behavior can help account for the distribution and redistribution of volatile gases at the lunar surface. Diurnal temperature variations influence the release and condensation of the gases from the regolith. *In situ* measurements during Apollo (*Hoffman et al.*, 1973) detected H_2, ^4He, ^{20}Ne, ^{36}Ar, and ^{40}Ar at night, but only ^4He in the daytime, when backgrounds from anthropogenic input were high. O_2 and CO_2 were not detected, nor were Na and K, which have been observed telescopically. Although increased sensitivity could lead to some improvement over Apollo measurements, the greatest gain could come from having less activity at the site of the instrument.

3.2.2. Mars

Many of the most critical questions about Mars addressable in the near future revolve around the history of water. When was there water on the surface and what happened to it? Has a portion of the atmosphere been lost, and if so, when? Isotopic and evolved gas analysis can provide important information. In particular, only through isotopic measurements can the question of "when" be definitively answered. Most of our present knowledge of Mars (*Kieffer et al.*, 1992) comes from two sources: the Viking mission, which included two orbiters and two landers; and the SNC meteorites, 11 rocks that are believed to come from Mars. Detailed relative chronologies of martian surfaces have been determined from Viking images, and accurate crystallization ages of some of the SNC meteorites have been determined, but the relationship of the two cannot be determined. Absolute chronologies based on extrapolation of the lunar cratering flux give ages that vary by as much as 2×10^9 yr for some surfaces (Table II of *Tanaka et al.*, 1992). Thus surface ages, even if uncertain by as much as 10–20%, would be significant. Several different kinds of surface ages might be adequate. Crystallization ages of lava flows on terrains of known relative age could be used to calibrate the crater-based age scales, but cosmic-ray exposure ages (based on ^3He or ^{21}Ne) of young ($<10^9$ yr) surfaces might be as useful. Alternatively, it might be possible to determine directly the ages of aqueous alteration products. The problems involved with various approaches to such ages will be discussed in section 3.4.

Mass spectrometers on the Viking landers measured the abundances of eight elements, including the isotopic abundances for most of them (to precisions of 5–50%). The $^{15}N/^{14}N$ and D/H ratios are much higher than terrestrial, indicating mass-dependent atmospheric loss processes. The radiogenic noble gas isotopes ^{40}Ar and ^{129}Xe are also enriched relative to ^{36}Ar and ^{132}Xe respectively, although the exact

ratios are only known to the 20% level for Ar and 50% level for Xe. The isotopic composition of C, O, and Ne were reported to be within 5% of terrestrial. Much more precise measurements are available from gas trapped in glassy inclusions in the SNC meteorite EET 79001. The relative elemental and isotopic ratios for N and the noble gases match the less-precise Viking measurements over 10 orders of magnitude in gas abundance, providing the strongest argument that these meteorites are indeed from Mars. The elemental abundance of He and the isotopic composition of O have been measured telescopically, but the O measurement is only marginally consistent with the Viking measurement (they differ by 10%, but each has 5% quoted precisions). Additional measurements of the atmospheric composition would have to be considerably more precise than Viking to be valuable. Percent-level measurement of $^{18}O/^{16}O$ would be helpful in determining the interaction of the atmosphere with the polar caps and surface, and more accurate noble gas measurements would allow for more refined models of atmospheric evolution.

Measurements of the molecular composition of evolved gases, both from martian regolith or from martian polar caps, would be helpful in constraining current interactions between these samples in terrestrial laboratories, including many that would be difficult or impossible to apply *in situ*. One of characteristic features of the SNC meteorites is their O isotopic composition, but is only diagnostic if abundance ratios of all three O isotopes (^{16}O, ^{17}O, and ^{18}O) can be measured to better than 0.1% precision (preferably 0.01%). However, 1% level accuracy of the $^{38}Ar/^{36}Ar$ or $^{129}Xe/^{132}Xe$ ratios would be nearly as good.

3.2.3. Comets

Comets are very small (less than 10 km radius) bodies that contain ices of various types. They are thought to have remained in a very cold state since their time of formation and thus may be samples of the most primitive materials known in the solar system. As a result, comets are considered crucial for understanding the origin of the solar system and of life (*COMPLEX*, 1994, p. 188).

Comets contain molecular species more volatile than water ice, whose overall composition may reflect that of grains derived from the parent molecular cloud that was the solar system's progenitor. Comparison of a complete sample of molecular species, coupled with a determination of the mechanisms by which they are bound into the water ice and organic phases, will provide a dataset of extraordinary value in characterizing the nature of the forming solar system. Further, it will provide a strong set of constraints on the concept that comets or related outer solar system objects supplied much of the volatile inventory of the terrestrial planets early in the solar system's history.

Analyses of gases in cometary comae have been made both from groundbased observations and from spacecraft at Comet P/Halley. In order to constrain the origin of the cometary

grains, however, it is necessary to determine the phase from which the gases are evolved. For example, we know that comets contain CO, but it is critically important to understand if the CO is present as a pure ice phase, is trapped in a clathrate hydrate, or is absorbed on amorphous water ice. Each of these possibilities puts different constraints on the temperature and pressure environment in which the cometary grains formed. By knowing the temperature at which these gases are evolved from the comet, it is possible to determine the host of the CO_2. This important scientific objective of understanding the pristine ice phases requires a lander-based instrument that can collect the pristine ices from beneath the surface and determine both the composition of the evolved gases and their release temperature.

In addition to understanding which gaseous compounds are associated with which phases in the comet, it is important to determine their isotopic composition. Meteorites are known to have an isotopic composition of light elements, H, C, N, and O, that differs substantially from normal terrestrial values and in fact differs between different phases in the same meteorites. It is very important to determine the isotopic composition of these elements in comets and especially to determine the isotopes both in different compounds and in the same compounds from different hosts. For example, we want to know if the $^{13}C/^{12}C$ ratio in CO associated with amorphous ice is different from that of CO associated with clathrate hydrate or of CH_4 associated with clathrate hydrate.

3.2.4. Asteroids

The asteroids are a diverse set of objects, all less than 1000 km in diameter, ranging from primitive asteroids that are believed to contain ices to differentiated bodies (*Binzel et al.*, 1989). We believe we have samples of many asteroids in our collections of meteorites, but, with few exceptions, we don't know which meteorites sample which asteroids (*Wetherill and Chapman*, 1988). Hence, one of the most crucial questions about asteroids is that of the connection between meteorites and asteroids, and that is not readily amenable to isotopic analysis—the precision needed to measure isotopic ratios definitively (e.g., all three isotopes of O to 0.01%, *Clayton et al.*, 1991) can probably only be obtained by returning a sample, which may not be prohibitively expensive anyway for these low-gravity objects. On the other hand, there are some types of asteroids that apparently contain hydrated minerals, although these types are not common near the Earth and may not be well represented in meteorite collections. These asteroids might very profitably be studied by some of the techniques used for studying comets, especially evolved gas analysis, which could determine the abundance of water and other volatiles, which are of both scientific and resource interest.

3.2.5. Venus

Surface. The venusian surface has been studied by seven successful Soviet landing craft, three American and several Soviet atmospheric probes, and the Magellan synthetic aperture radar, among other projects. Each lander succumbed to the harsh conditions on Venus after roughly an hour of operation, which was enough time to transmit television images, engineering data on the surface rocks, and X-ray-fluorescence and γ-ray spectrometer analyses of surface rocks. The surface (at least in the lowlands) is dominated by mafic volcanic rocks (*Barsukov et al.*, 1986). The surface is much too hot to allow aqueous weathering or the existence of most common types of terrestrial hydrated minerals on Venus, but surface-atmosphere chemical interactions (weathering) does occur, with the production of minerals such as calcite and anhydrite, which appear to be abundant on Venus (*Barsukov et al.*, 1986; *Fegley et al.*, 1992; *Kargel et al.*, 1993). Some version of evolved gas analysis would be the most effective way to determine the actual weathering products present, and isotopic analysis would constrain some of the details.

Cratering statistics indicate that Venus may have experienced global volcanic resurfacing around 300 m.y. ago, and that it has been relatively quiescent ever since. This inference carries broad implications for the nature of mantle convective dynamics in Venus and perhaps in the other terrestrial planets (*Schaber et al.*, 1992). Testing this hypothesis is one of the key scientific objectives for Venus (*COMPLEX*, 1994, p. 96).

Ages for carefully selected volcanic rocks from perhaps five terrains, even if only accurate to 10%, could readily test the global resurfacing model. Aside from the serious engineering hurdles that would have to be passed to have a spacecraft survive on the surface, the success of any attempts to produce isotopic ages or useful stable isotopic measurements for venusian rocks depends on the degree to which certain minerals on Venus may have been closed to significant isotopic exchange and reequilibration. The high surface temperatures and the occurrence of carbonate-sulfate weathering might tend to cause some elements in some susceptible minerals to be unreliable for useful isotopic work. Unfortunately, Ar can diffuse out of virtually every mineral (*Head and Swindle*, 1995), and cosmic-ray exposure ages will not be applicable because of the shielding from the atmosphere. The behavior of isotopic systems under metamorphic conditions on Earth suggest that many other parent and daughter elements widely used in radiometric dating methods (U, Pb, Lu, Hf, Sm, Nd, La, Ba, Re, and Os) are probably fairly immobile on Venus even in the face of high temperatures and severe chemical weathering, but these will only help if techniques to precisely measure their isotopes can be developed. To get a rough idea of the magnitude of changes in isotopic ratios expected on Venus due to radiogenic growth and the accuracy with which isotopic measurements would have to be made to provide scientifically useful results, we have calculated radiogenic growths for three isotopic clocks, using trace-element abundances typical of terrestrial samples analogous to two model rock compositions expected on Venus, olivine leucitite (Venera 13) and mid-ocean ridge basalt (Vega 2). In 300 Ma (*Schaber et al.*, 1992), the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios

would increase by less than 0.1%, while the $^{206}Pb/^{204}Pb$ ratio would increase by a few percent. Measurement precisions would have to be an order of magnitude better than the size of these increases to get 10% precision on ages.

Atmosphere. Venus' atmosphere has been studied by several spacecraft, most notably the armada of four spacecraft from two different space agencies (Pioneer Venus Orbiter and Multiprobe and Veneras 11 and 12) that arrived in December 1978, each carrying a mass spectrometer and gas chromatograph. This unique complement of highly sophisticated instruments has provided a wealth of information on the composition of the Venus' atmosphere (*Hoffman et al.,* 1980).

Isotopic compositions obtained by various instruments are included in Fig. 3.1. It was not a surprise that CO_2 is by far the dominant constituent, but the $^{40}Ar/^{36}Ar$ ratio (300x lower than Earth and >2000x lower than Mars) and D/H ratio (100x higher than Earth) were surprises. In general, much is known about the composition and isotopic ratios of the Venus atmosphere, but the error bars in many cases are quite large (±50%) and there remain some disagreements between the results from the various instruments. Future studies of the Venus atmosphere need to address the precision of the measurements, verify that the D/H ratio is indeed 2 orders of magnitude different from Earth, and determine some of the ratios of rarer isotopes that could be diagnostic of the origin and evolution of the atmosphere, including $^{20}Ne/^{22}Ne$, $^{38}Ar/$ ^{36}Ar, and the major isotopes of Kr and Xe. In addition, we need to measure the oxidation state (i.e., O_2 abundance or CO/ CO_2 ratio) in the lowest part of the atmosphere, and obtain more definitive data on the interactions between surface materials and S- and Cl-bearing compounds in the lower atmosphere.

3.2.6. Mercury

Mercury is the least well known of the terrestrial planets, with only Earth-based observations and the Mariner 10 flybys (*Vilas et al.,* 1988). Mariner 10 did not carry any mass spectrometers, so no isotopic information is available. Mariner 10's airglow spectrometer did identify H, He, and O in the tenuous mercurian atmosphere, and Na and K have been identified telescopically. If further flybys or a rendezvous mission precede any surface missions, the questions addressable by isotopic and evolved gas analysis can be more finely honed. For the moment, there are some obvious fundamental questions that can be addressed.

The foremost question at the moment is the composition and origin of the radar-bright polar caps. Analysis of gases evolved by heating of a sample from a polar region could address the elemental and molecular composition of the polar cap, and provide isotopic information (for example, D/H ratio of water ice) that could constrain the mode of origin.

The age of the mercurian surface is completely unknown, although it is believed to be quite old. Since it is the innermost planet, determining the ages of surfaces by determining the crystallization ages of rocks would provide a calibration point

for cratering rates throughout the inner solar system. In addition, determining the ages of rocks from the youngest surfaces would determine how recently volcanic activity occurred, which in turn is crucial for understanding the evolution of the interior.

Mercury's atmosphere is most similar to that of the Moon, and measurement of the elemental and isotopic composition of the mercurian atmosphere could address the same sort of questions: What is the source of the atmosphere? Is some of it degassed from the interior? How does it vary through the mercurian day?

3.2.7. Icy Satellites and Pluto

Some of the most important questions about the solar system's origin can only be answered with studies of icy satellites of the gas giants, and some of these questions will require isotopic investigations of ices by landed spacecraft. We do not anticipate these types of missions being launched any time in the next decade, but the technology to conduct these sorts of missions seems not much more than some combination of the technologies developed for the Galileo and Cassini orbital tours, *in situ* comet analyses, and, if they can be developed, Mars missions involving *in situ* isotopic dating.

Investigations of stable isotopes in undifferentiated primitive icy satellites and their planets' atmospheres could teach us a great deal about compositional fractionations and other formational processes in the circumplanetary nebulae and about the differentiation of the gas giants and their massive atmospheres. Similarly, analysis of the elemental and isotopic composition of the atmospheres of those bodies with tenuous atmospheres, such as Triton and Pluto, could reveal much about the origin and evolution of those atmospheres and their parent bodies. Other problems addressable by isotopic analysis have more restricted pertinence to the icy satellites themselves. Many of these studies are of a reconnaissance nature, so they could produce useful data with lower precisions than that required for instruments flying to planets for which we already have some knowledge.

Given the much greater distances and the double energy penalty that would be involved for a sample return mission, the chronology of outer planets and their satellites may be best addressed by isotopic measurements from a robotic lander. Models require anything from millions to hundreds of millions (or even billions) of years for formation of giant planets and their satellite systems. Convincing evidence of the duration of accretion of primitive icy satellites would provide an important constraint on solar system formation. Similarly, absolute calibration of cratering ages on even a single icy satellite would have similar value in providing absolute calibration in the inner solar system, since the relationship of the various impacting populations is not definitively known. *Kargel* (1992) has shown that some cryovolcanic flows could contain enough K and Rb to permit radiometric dating, if appropriate techniques can be developed.

Perhaps the most significant use of isotopic and evolved gas analyses in the outer solar system might be investigations of organic chemistry on Titan. These investigations could have broad implications for prebiotic chemistry on Earth and elsewhere in the universe, one of the key concepts developed by *COMPLEX* (1994). The Cassini mission and comet missions discussed above will lay the groundwork for any future Titan missions.

3.3. POTENTIAL INSTRUMENTS

In this section, we review many of the instruments that could potentially be used to answer the questions listed in the previous section. We begin by discussing a variety of mass analyzers, and then some of the more promising techniques for getting ions to the mass analyzer. In this chapter, we emphasize techniques leading to mass analysis, although we recognize that, for some evolved gas analyses, a mass analyzer is not required.

3.3.1. Mass Analyzers

Table 3.1 lists the mass analyzers that have been or are planned to be flown to study planetary atmospheres. The U.S. has never flown a mass analyzer for solids, although the European Giotto mission (PUMA) analyzed dust particles

from Comet P/Halley, and the Russian Phobos mission had analyzers (LIMA-D and DION) scheduled to be used on the surface. These and other mass analyzers are described below; Table 3.2 lists the principal advantage of each.

Magnetic sector-field. Magnetic sector-field mass spectrometers have been the mainstay for analyses of planetary atmospheres (Table 3.1). They typically consist of an ion source, a magnetic momentum analyzer, and a detector, which usually consists of channeltron electron multipliers or microchannel plates (Fig. 3.2). Pulse counting circuits accumulate the data and store them for transmittal to a data handling system. Ions are formed by electron bombardment of the source. The resulting sensitivity at 250 µA emission current is of the order of 10^{-5} to 10^{-6} amps/torr, consistent with the detection and signal processing dynamic range. Electron energy can be varied (e.g., from 15 to 70eV) to assist in determining molecular and atomic composition by changing the resulting cracking patterns and charge states. Ions are accelerated from the source by voltage (V_s) and collimated into a beam. The beam then traverses a magnetic field (strength B) that bends it through a suitable angle (usually usually 90° or more), and is focused onto a collector slit. The acceleration, a, of an ion of charge q and mass m in the magnetic field is

$$a = [q(v \times B)]/m \qquad (3.1)$$

where v is the velocity, which is in a plane perpendicular to the magnetic field. Since the acceleration for a radius of curvature r is

$$a = v_2/r \qquad (3.2)$$

the mass-to-charge ratio of ions that successfully traverse the curved path of the mass spectrometer flight tube is a function of the magnetic field strength and the ion momentum, the latter being varied with time to scan the mass spectrum. Most spacecraft mass spectrometers have used multiple collectors, e.g., ion beams with three different path radii focused simultaneously on three collector slits, to cover a wide mass range with a fairly narrow voltage sweep range. This way, multiple mass peaks (three, in the example) may be monitored simultaneously.

TABLE 3.2. Principal advantages of each type of mass spectrometer.

| Instrument	Principal Strengths
Magnetic, single-focusing	Simple operation, no RF voltages. Very good mass resolution with proper ion sources. Simultaneous collection of 2–3 mass peaks. Very high sensitivity.
Magnetic, double-focusing mass spectrograph	Excellent mass resolution. More complex operation. Very high mass-rejection ratio. Simultaneous collection of a wide range of mass peaks.
Quadrupole, linear	Good mass range. Accepts positive or negative ions in same instrument. No magnetic field. Highly efficient in ion transmission, but at a fairly low mass resolution. Ion energy independent.
Quadrupole ion trap	Very compact and low mass. Very high mass resolution. Very high sensitivity. Large mass range. Very rapid analysis. Possible to do mass analysis on specific mass species (MS-MS technique).
Time of flight	Wide acceptance angle. Very rapid analysis. High sensitivity.
Wien filter	Simultaneous collection of range of mass peaks. No RF voltages.
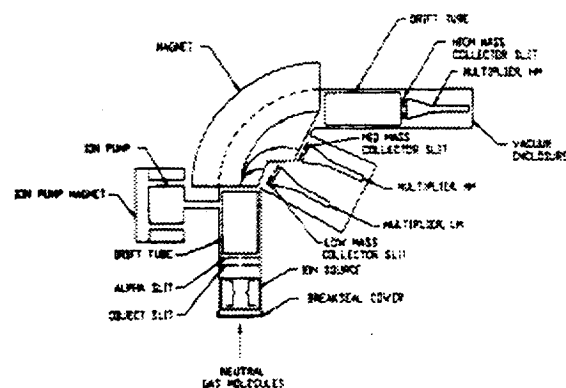
Fig. 3.2. Single focusing mass spectrometer, with collectors for simultaneous analysis of three masses.

Behind each slit is a high-counting-rate channeltron electron multiplier that monitors the mass spectrum as the ion beams are scanned across the collector slits. When counting rates are plotted as a function of V_s, equivalent to ion mass, a mass spectrum is produced depending on the form of V_s. One typical operating mode is to step from peak top to peak top, which results in an efficient use of both telemetry band width and spectral scan time. Magnetic mass spectrometers may employ an electrostatic analyzer in tandem with the magnetic analyzer. Such a configuration (Fig. 3.3) has double-focusing properties (both angle and energy focusing). These will generally exhibit higher mass resolution than single focusing magnetic analyzers but are more complex to operate. Focal plane detectors, such as microchannel plates, may be used to simultaneously collect many ion peaks, thus making the instrument a spectrograph.

Quadrupole mass filters. Strictly speaking, the quadrupole is a mass filter rather than an analyzer because it transmits ions having only a small range of m/z values, and there is no mass dispersion or focusing as in magnetic analyzers. Thus, it is analogous to a narrow-bandpass electrical filter that transmits signals within a finite frequency bandwidth, and a trade-off is made between transmission and resolution. The conventional quadrupole mass analyzer (Fig. 3.4) utilizes four parallel cylindrical or hyperbolically shaped rods. The rods are long relative to the inner "kissing circle" diameter, to minimize fringing fields on the active length of the rods. A quadrupolar potential is established by applying a time-varying potential $+\Phi$ and $-\Phi$ on alternate rods (at the four locations $\pm x$ and $\pm y$), where

$$\Phi = (U_0 + V_0 \cos \Omega t)[(x^2 - y^2)/r_0^2] \qquad (3.3)$$

(*Paul et al.*, 1958) for a dc component U_0, and an rf component V_0 of frequency Ω. The ions are injected (in the z direction) into the central "flip-flopping" saddle-potential region, and only those ions having the correct mass are transmitted to the exit aperture without sliding into one of the rods. The ion trajectories in the x and y directions are governed by the Mathieu equations

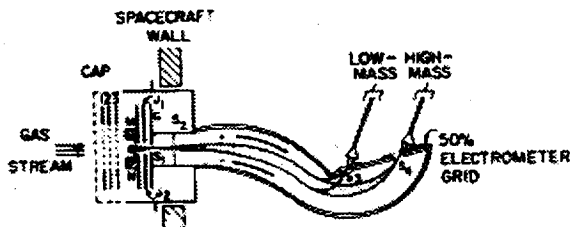$$x^2 + (a - 2q) \cos 2\xi \, x = 0 \qquad (3.4)$$

Fig 3.3. Schematic drawing of a Mattauch Herzog double-focusing mass spectrometer (*Nier et al.*, 1973). The cap shown by the dotted line is ejected in orbit, exposing the ionizing region to the gas stream. Two detectors are shown, but the focal plane could be covered by a microchannel plate detector.
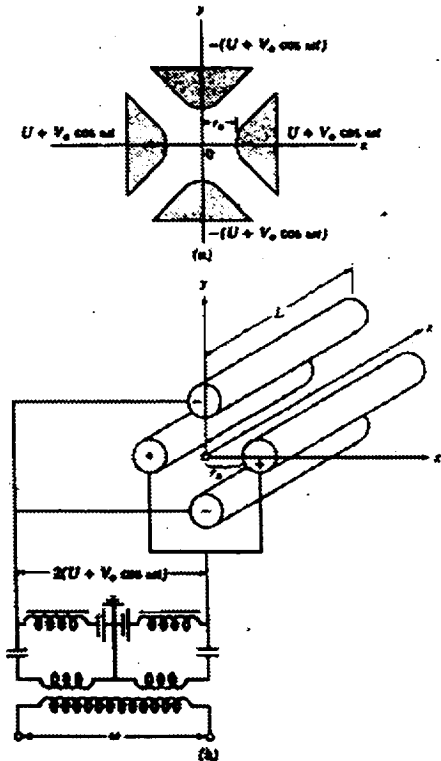

Fig. 3.4. The quadrupole mass filter (*White and Wood*, 1986) showing idealized electrode configuration and cylindrical rod assembly. An ion source is placed in front of the rods and a channeltron electron multiplier usually follows the rods.

where the parameters a and q determine the region of stable solutions to equation (3.4).

A mass spectrum is obtained by sweeping U_0 and V_0 linearly (at a fixed Ω), and detecting the transmitted masses (one at a time) at the exit plane with a Faraday cup or particle multiplier. The resolution of the device depends on the rod geometry r_0, frequency Ω, rod length, and axial and radial ion injection energies. In the original publication (*Paul et al.*, 1958), resolutions $m/(\delta m) = 1500$ were reported, sufficient to resolve ^{16}O (15.9949 dalton) and $^{12}ClH_4$ (16.0313 dalton). NASA flight mass spectrometers for planetary aeronomy are of the quadrupole type with hyperbolic rods. The resolution is approximately 0.3 dalton, with narrow wings on each peak so that two adjacent masses can be resolved if their intensity ratio is 10^4–10^5 (*Spencer et al.*, 1985; Niemann, Cassini penetrator mass spectrometer). This is vital for exploring the full density range of trace ions and neutrals present in a complex planetary atmosphere. A miniature quadrupole array, with sixteen 25-mm-long rods, weighs less than 30 g (including ionizer and detector). The advantages of a well-designed quadrupole analyzer are sensitivity, good mass range and resolution, dynamic range (10^6 or better), and mass rejection (10^4 or better for adjacent masses). Disadvantages are that the transmission is mass dependent, and is a strong function of desired resolution.

Time-of-flight analyzer. A conventional time-of-flight (TOF) mass spectrometer consists of an ion source, a long field-free flight tube, and particle detector (*White*, 1968). Timing gates (akin to traffic lights on a boulevard) are placed at each end of the flight tube. Ions from the source have a relatively narrow energy distribution, usually of width 0.5–1.0 eV. For high resolution a narrower energy distribution is needed. This may be done by use of an energy "predisperser" such as a Bessel box or an electrostatic analyzer. The ions are accelerated (usually to 10–1000 eV) toward the first gate, which is opened for a short time "δ" by a square pulse, and a packet of ions enters the tube. Ions with different masses have different velocities and traverse the tube with different flight times T. The opening time of the second gate (traffic light is "green") fixes the mass of the ions transmitted and detected. The relation between the flight time T, length of tube L, and injection energy E is just

$$m = 2E (T/L)^2 \qquad (3.5)$$

where T/L is (particle velocity)$^{-1}$.

Advantages of the TOF method are its large mass range, sensitivity (no limiting slits), and relative simplicity of construction. The principal disadvantage is that the duty cycle D, the product of the cycle repetition time and the time (δ) that the gate-opening pulse is "on," is usually less than 1%. One is limited in the pulsing frequency by mass-aliasing effects: A faster particle from a later pulse can catch up with a slower particle from an earlier one. To obviate this, one may install a third traffic light in the tube, so that ions must have traversed two timed gates after the opening gate. This arrangement eliminates aliasing velocities to an order sufficient to disallow expected overlapping velocities in the sampled plasma. One may accommodate many pulses in the flight tube, and hence D can be increased to about 10% (*Martus et al.*, 1993). Another smaller disadvantage is the need for faster risetimes and narrower pulsewidths if one needs to go to shorter flight tubes to miniaturize the TOF instrument.

Laser ablation mass spectrometers. In laser ablation mass spectrometers, a tiny spot on the surface of a sample is ablated by a short laser pulse. Surface material is converted into a low-energy plasma, and some of the resulting ions, expanding away from the ablation point, travel through an electrostatic "reflectron" and impact a microchannel plate detector (MCP). The electrostatic fields in the reflectron (Fig. 3.5) are designed to cancel energy dispersion of the ions over a broad energy range covering the peak of the ion distribution, resulting in ion time-of-flight (TOF) from the point of ablation to the MCP that is independent of ion energy, and proportional to the square root of ion mass. For typical compact laboratory instruments, the TOF ranges from a few microseconds (for H) to <100 μs (for >200 amu), and thus the MCP current as a function of time after the laser pulse provides a mass spectrum of the surface material. This current can be digitized with high accuracy and time resolution, providing isotopic mass resolution for every element. A laser ablation mass spectrom-
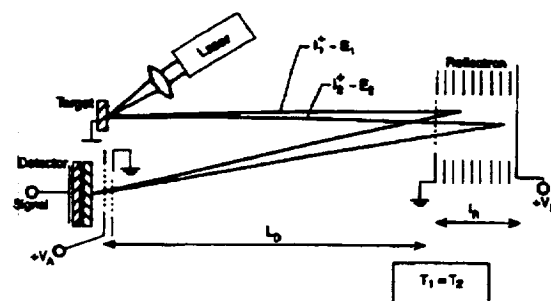

Fig. 3.5. Schematic diagram of a laser ablation time-of-flight (TOF) mass spectrometer. A pulsed (<10 ns) laser ablates a 10–30-μm spot on the target, creating energetic plasma ions, some of which follow trajectories such as those for ions labeled I1 and I2. Ions of the same mass but different energies (for energies between VA and VR) experience TOF dispersion in the free-flight region LD that is compensated within the reflectron region LR; TOF then depends only on the mass. Multistage reflectrons are frequently used, and many configurations of the instrument are possible.

eter was flown on the Phobos mission (LIMA-D). Modern instruments are small, low power, and low mass (a few kilograms), well suited for mission to small bodies in the solar system, and provide quantitative analysis for all elements and isotopes present in a sample down to levels below 100 ppm.

Quadrupole ion trap. The quadrupole ion trap analyzer (QTA) is a form of quadrupole mass analyzer that employs three electrodes, two of them end-caps that are normally at ground potential and between them a ring electrode to which DC and RF voltages are applied (Fig. 3.6). After ionization, ions are trapped in orbit in the RF field until measurement is desired. The RF voltage, which has a frequency of the order
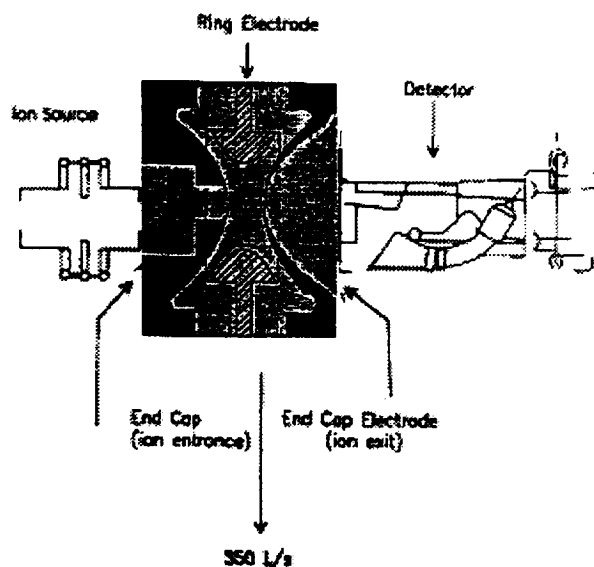

Fig. 3.6. Schematic of a quadrupole trap analyzer (QTA). The ring electrode and end caps are cylindrically symmetric about a horizontal line from the ion source to the detector.

of 1 MHz, causes the ions to undergo stable oscillations between the electrodes, provided their mass-to-charge ratio falls within appropriate limits. Otherwise, their motion is unbounded and they quickly leave the trap. To extract the ions, the amplitude of the RF voltage is increased, causing ions of successively increasing mass to be ejected through one of the end caps into an electron multiplier. The signal from the electron multiplier, typically a channeltron, forms a mass spectrum from which the identification and relative abundances of the gases that were sampled by the QTA are determined. The design of the ion trap analyzer allows for an unprecedented reduction in the weight of the mass spectrometer. A prototype of the analyzer, which fits in the palm of a hand, weighs <100 g, which is less than 10% the weight of a conventional analyzer. The trap function, in addition, provides an unparalleled increase in sensitivity and mass resolution.The QTA has not yet been flown in space but at least two groups are trying to develop it in the near future.

The Wien filter. The Wien filter is based on the principle of an ion of the correct velocity traversing a region of crossed electric and magnetic fields, the ion's injection velocity being perpendicular to the crossed fields. At the tuned velocity, the electrical force $q\mathscr{E}$ will just match the magnetic deflection $qv \times B$, and the ion will pass undeflected. All other ion velocities will be deflected in a plane defined by the incident ion direction and the direction of $\mathscr{E}$. This tuned velocity is simply given by, for fixed particle injection energies E,

$$v^2 = (\mathscr{E}/B)^2 = 2E/m \qquad (3.6a)$$

or

$$m = 2E(B/\mathscr{E})^2 \qquad (3.6b)$$

A spatially extended detector (microchannel plate strip, charged-couple device, or multianode detector) may be used at the exit to detect groups of masses simultaneously. Good homogeneity of the magnetic field is required. Any single-particle detector must be shielded (to less than about the 0.005 tesla level) from the B field of the filter.

Advantages of the Wien filter are its mass multiplexing (10 masses, say, detected simultaneously). Disadvantages are the need to have accurately aligned and homogeneous $\mathscr{E}$ and B fields, and to use a shielded particle detector without disturbing the field homogeneity at the detection plane. Peak broadening effects, such as beam shear in the $\mathscr{E}$ field, have not been characterized yet.

3.3.2. Extraction and Inlet Systems

Evolved gas analysis via gas chromatography (GC) is a technique that has been used for years in the laboratory to analyze gaseous mixtures. There are two aspects of the technique: separation and detection.

Separation. The separation of the compounds in the gas is based on the principle of establishing an equilibrium between a mobile phase (the gas) and a stationary phase (a solid or liquid). The gas flows through a column that is either packed with, or has its walls coated with, the stationary phase. An inert carrier gas, often N or He, constantly flows through the column. When a gas mixture is to be analyzed, a small amount (relative to the volume of the column) is introduced at the head of the column and the carrier gas forces the gas mixture through the column. Compounds that are strongly adsorbed by the stationary phase are removed from the gas mixture, while those that are not adsorbed pass directly through the column. The gases that are adsorbed are then released back to the pure carrier gas that follows the gas-mixture spike. These gases are again adsorbed a little further down the column and released a short time later as more pure carrier gas flows past. This process repeats itself many times as the strongly adsorbed gases make their way down the column. At the end of the column the gases exit, separated by the degree to which they were adsorbed; the first gases out are those that were not adsorbed, followed by those with progressively greater affinity for the stationary phase.

It should be obvious that one stationary phase is not suitable for separating all compounds since the nonadsorbed compounds are not separated; they move through the column as if it were an inert pipe. Depending on the compounds of interest, several columns are generally used. For example, one might be used for polar compounds, e.g., water and ammonia, another for nonpolar compounds, e.g., hydrocarbons, and a third for the "permanent" gases, e.g., N, O, and CO.

Old technology columns were typically several millimeters in diameter and took about 5–10 min to process a gas sample. This time requirement implies that one could not monitor gases that were changing rapidly with time. Newer columns are a fraction of a millimeter in diameter and can process a mixture in tens of seconds.

Detection. The detectors used to determine the time of elution and amount of the compound fall into two categories: specific and nonspecific. For mixtures of simple compounds, a nonspecific sensor is adequate; the time of elution is diagnostic for the compound. For more complex compounds, several different compounds can have similar elution times. In this case, a specific detector, usually a mass spectrometer, is used. The combination of a GC and a MS is useful for complex mixtures, as GC spectra with a nonspecific detector are difficult to interpret, and the mass spectrum of a non-separated mixture may also be too complicated to interpret. A disadvantage of coupling an MS to a GC, especially with high-performance columns, is that the elution peak of a compound of interest will be very narrow (fraction of a second), and there may not be sufficient time to get adequate statistics to determine isotopic ratios. A common nonspecific sensor relies on differences in thermal conductivity between the eluting gases and the carrier gas. Thermal conductivity can be measured with a hot thermistor, and changes in conductivity are proportional to the concentration of elutant. Another nonspecific sensor relies on differences in electrical conductivity of the gas when ionized. An example of this

detector is the metastable ionization detector (MID). In the MID, a low-energy β-emitting radioisotope inside the detector activates the He carrier gas to an excited state. The eluted molecules become ionized via collisions with the activated He, and the current in the detector is proportional to the concentration of the eluted compound. The latter detector is more sensitive, but the electronics are more complex.

Evolved-gas analysis of nonseparated gases via compound-specific detectors. For very simple mixtures, or for applications where concentrations of only a few species are needed, it is possible to include specific chemical sensors for each compound of interest. For example, to determine the composition of breakdown products of clay minerals and carbonates such as might be expected on Mars, it is possible to simply include only a sensor for water and one for CO_2. Most compound-specific detectors are designed so the compound of interest sets up an electrochemical potential across suitable electrodes, much like in a pH meter. Most compound-specific electrodes are also sensitive to other compounds (to varying degrees), and sensors for a number of specific compounds may be required to yield unambiguous analyses. For water, other types of sensors can measure relative humidity or dew point. These devices are much simpler than a GC, but require that one know beforehand (and without doubt) the nature of the solids to be analyzed.

Lasers as a means of extraction. Lasers produce a very stable power density (W/cm^2) and may operate during day or night. The average and peak power requirements must be determined along with the duty cycle. The selection of the laser must be based on (at least) the following criteria: (1) absorption of laser radiation by the material, (2) a thermal model, and (3) characterization of the laser.

Using these absorption properties as criteria for selection, lasers for potential use as a means of extraction from silicate surfaces include ion lasers like Ar and Kr (UV), CO_2 (10.6 mm, IR), and the fourth harmonic of the Nd:YAG (266 nm, UV). The ion lasers are more expensive and less efficient.The laser characteristics determine the spot size that can be heated to a required temperature, and also whether the laser is continuous or pulsed. The spot size is determined by the divergence of the beam and can be calculated. With the laser at a distance of 10–100 cm from the sample, and typical laser beam parameters, a spot size of 4–7 mm can be achieved without lenses, and a spot size of 400–8000 mm can be achieved with a single lens. Larger beam diameters can be achieved by using beam expansion techniques.

Laser ablation. Pulsed lasers, such as the Nd:YAG, deliver an extremely high power density, >10^9 W/cm^2, for a short duration, 5–10 ns, to the sampled spot. This creates a plasma ball of ionized target material at the focused spot. Mass spectrometers may detect the ablated elements at a distance of up to several tens of meters. The release of ionized elements by this laser is rather indiscriminant with regard to siting of an element within the lattice region being ablated.

TABLE 3.3.   Laser extraction systems.

	Ablation	Desorption
Maximum range	Several tens of meters for major elements	<1 m
Laser type	Nd:YAG 1.06 μm	CO_2 10.6 μm
Power density	10^9 W/cm^2	800 W/cm^2
Spot size	1–2 mm	400 μm (focused 2–4 mm beam)

Thus major elements would be expected to dominate the release spectrum. Laser ablation techniques have been incorporated in planetary surface instrument designs in combination with spectroscopy (LIBS, *Blacic et al.*, 1993) and mass spectrometry (LIMA-D, *Sagdeev et al.*, 1986; and *DeYoung and Situ*, 1993). A pulse repetition rate of 0.1–0.2 Hz may be reasonable. Typical parameters are summarized in Table 3.3.

Laser desorption. The CO_2 continuous wave (CW) laser operating at IR wavelengths imparts its energy over a longer duration, allowing for a controlled heating of the sample. Gases and other elements may be thermally desorbed from solid surfaces under vacuum conditions in this fashion. The desorbed gases may be measured with a mass spectrometer. This approach has the advantage of providing the potential for stepwise release of gases from the sample, allowing for *in situ* component separation. Trace amounts of trapped gases may be released selectively by moderately exciting and expanding the lattice of the target material. Thus, interference from major elements may be avoided, but the mass spectrometry must occur relatively close to the target to detect the trace amounts of released gases.Thermal model calculations suggest that small lasers with only small peak power consumption (~10 W) may be adequate for *in situ* heating of silicate materials. To heat a 1-mm^3 spot on quartz to a temperature of ~950°C within 1 s requires a power density of 160 W/cm^2. Taking into account heat loss and other considerations, a laser that can deliver several hundred Watts per square centimeter should be sufficient. A 10-W CW laser with a 4-mm beam has an unfocused power density of about 80 W/cm^2 or, when focused to a 400-mm spot, about 8000 W/cm^2. This is a theoretical calculation based on ideal conditions. In practice, however, the achievable power density at the focused spot could be down by a factor of 2–4. Also, in order to calculate the actual energy transfer to the sample, the losses at surfaces of the focusing lens and the sample itself have to be accounted for. This will introduce another loss of a factor of about 5. The practical transferred power density will therefore be about 800 W/cm^2, sufficient to carry out heating experiments.

The duty cycle and/or repetition rate determines the average power delivered to the sample and the "off" time. The 10–20-W peak power requirement would be excessive if continu-

ous operation were required. The duty cycle, however, need not be continuous. Periodic "zaps" with durations of only a few seconds may be sufficient for surveys. Thus, the average power required could be significantly lower than the peak power, with the appropriate choice for the period. The operation of pulsed lasers normally gives high peak power, but a low average power. Assuming a 10-ns pulse and a 0.1-Hz repetition rate, the pulsed Nd:YAG laser used for LIBS can deliver 180–1000 mJ of energy for an average power of 0.3–1.5 W (*Blacic et al.*, 1993). The duty cycle of the continuous CO_2 laser can mimic pulsed operation through power modulation. The "pulses" are longer (>1 s) due to the time required to ramp the power. From the thermal model discussed above, a focused continuous 10-W CO_2 laser could deliver enough heat energy to 1 mm³ of quartz in a 3-s "pulse" to reach 950°C, using an average power of 2–3 W and a 0.1-Hz pulse rate frequency during operation.

Chemical dissolution. In terrestrial laboratories, extensive chemical procedures are performed on much of the material slated to undergo isotopic analysis. Most of these procedures may be too complex for robotic probes to planetary surfaces, but it is possible that chemical dissolution, simply dissolving some readily attacked portion of a rock, might work. For example, halite can be dissolved in water or, at a slower rate, in methanol. On a robotic surface probe, this could be followed by mass spectrometric analysis of the gases released (e.g., Ar) and chemical analysis of the elements in the solution (e.g., K). *Wampler and Weaver* (1987, reported in abstracts by *Wampler and Hassanipak*, 1986, 1988) successfully used methanol to dissolve halite and stratigraphically obtain ages by the K-Ar method (see discussion in section 3.4.1). One of the few extraterrestrial bodies where salts might be expected is Mars, but if there are salts (e.g., evaporites) on Mars, their ages and composition would be of great interest. In terrestrial laboratories, chemical dissolution using HF has also been applied to U,Th-Pb dating of zircons (*Mattinson*, 1994), but the stronger acids and longer dissolution times required for silicates would make them more difficult to analyze *in situ*.

Inlet systems. A common problem of mass-spectrometer-based systems is interfacing the high vacuum of the ionizer-analyzer-detector portion (10^{-3}–10^{-4} torr in the ionizer, and 10^{-6} torr at the analyzer and detector) with a higher-pressure external atmosphere (to 760 torr). Common methods for dropping the pressure, and retaining the analyte sample, are (1) use of a variable-diameter (low-conductance) pinhole aperture; (2) use of a gas-chromatographic column with variable-conductance inlet valve, dropping the pressure as well as effecting a temporal separation of the analyte (*Carr*, 1984; *McFadden*, 1973; *Holland et al.*, 1994); (3) use of analyte diffusion through a hollow-fiber membrane (membrane-extraction mass spectrometry, MEMS) (*LaPack et al.*, 1991); (4) a molecular jet separator by which the pressure is dropped, and higher molecular-weight analytes are separated

from the lighter carrier gas, which may be, for example, the CO_2 on Mars or N_2 on Titan *(McFadden*, 1973; *Grayson and Wolf*, 1967; *de la Mora and Rosell-Llompart*, 1989; *Darrach and Chutjian*, 1995); and (5) use of a new type of "volcano" field-emission ionizer array in which the small opening of the volcano tip provides a low-conductance entry to the ionizer region, as well as acts as a sharp tip for field-ionization of the analyte-carrier gas mixture (*Spindt*, 1992).

In (4) the jet focusing and separation are most efficient when the ratio of analyte molecular weight to carrier-gas molecular weight is greater than or equal to about 10. Furthermore, a forepump is required to pump the intermediate nozzle-skimmer region. The devices in (2) and (5) are interesting in that they have been fabricated in miniaturized forms (micro-gas-chromatographic columns, and the microvolcanoes) for "matching" to future miniaturized quadrupole, ion-trap, Wien-filter, magnetic-sector, etc., analyzers.

3.4. AVENUES FOR FUTURE DEVELOPMENT

Having laid out the questions to be answered, and the general techniques that might be applied, what specifically could be done to improve our chances of answering those questions? One of the most intriguing possibilities is that a reliable technique to determine ages could be developed. We present discussions of four techniques that show varying degrees of promise, though none of the four has yet been developed sufficiently. In addition, we consider some instrumental requirements, those of precision, miniaturization, and survivability. Finally, we present some ideas about sample selection that need to be considered in any development effort.

3.4.1. Ages

One of the greatest scientific accomplishments of the Apollo program was to turn the study of the Moon's chronology into a quantitative discussion. Although geochemical clues to the Moon's evolution were available in the data from the Surveyors, ages were only determined because samples were returned. Nearly 30 years later, there is still not a single reasonably well determined absolute age from an *in situ* spacecraft measurement, and chronology is one of the chief justifications in arguments for sample return missions (*Drake et al.*, 1987). Given the importance of ages, we will discuss several potential techniques for determining ages with *in situ* instruments. In particular, we will set out the analytical precisions required for any of these techniques to work, as well as the interpretational problems that can be foreseen.

Radiometric dating methods are most powerful when the analyst can divide a sample into subsamples with the different ratios of the radioactive parent isotope to its daughter (*Faure*, 1986). If the parent and daughter elements share a common origin or equilibration time, parent/daughter abundances and ratios for these subsamples will be systematically related and
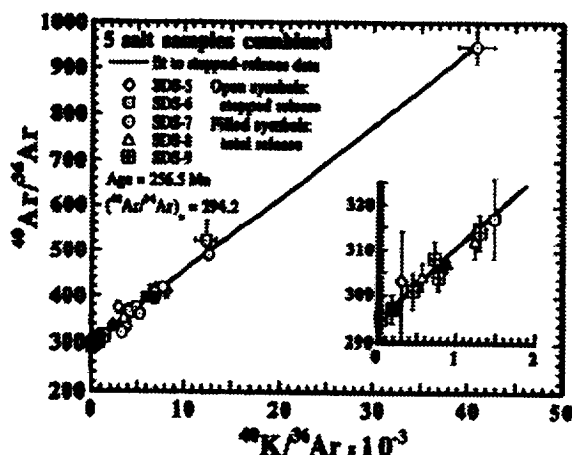
Fig. 3.7. Isochron diagram of $^{40}Ar/^{36}Ar$ vs. $^{40}K/^{36}Ar$ determined by K-Ar analysis with stepped dissolution of bedded salts (mainly halite) from the Permian Palo Duro Basin, Texas. Data points represent the Ar and K released by individual dissolution steps; numbers adjacent to the data points give the sequence of dissolution. The age is related to the slope of the isochron, and agrees reasonably well with the stratigraphic age of 266 Ma. The intercept gives the isotopic composition of trapped atmospheric argon. Data from *Wampler and Weaver* (1987).

form an isochron (Fig. 3.7), which defines the age of origin or equilibration. Thus, mineral separates from a single rock sample (i.e., portions of a rock prepared by physical separation of material) or multiple whole-rock samples from a cogenetic suite are commonly used in Rb-Sr, Sm-Nd, U-Pb, and other dating methods. Similarly, $^{40}Ar/^{39}Ar$ dating with stepped heating separates phases by their thermal stability, effectively yielding internal isochrons for rock samples. Potassium-argon dating with stepped dissolution (*Wampler and Weaver*, 1987) provides a similar separation by stability against chemical dissolution.

Potassium and argon extraction by dissolution. The chief benefit of K-Ar dating by stepped dissolution, if eventually applied to *in situ* dating of martian or other extraterrestrial samples, is that subsampling and extraction of K and Ar and can be done under ambient conditions with little expenditure of energy (grinding, heating, etc.). Unlike $^{40}Ar/^{39}Ar$ dating, stepped dissolution does not require neutron activation or gas release by heating; unlike some other methods, such as Rb-Sr mineral isochron dating, K-Ar dating with stepped dissolution does not require a mechanical or manual separation of mineral grains. Dissolution also allows all the major soluble components of a sample (the very components that give up their K and radiogenic Ar) to be analyzed; in general this is not possible with incremental release by heating.

In principle, the stepped-dissolution release method is applicable to almost any kind of rock. In practice, it works best for phases that are easily dissolved. Thus, it is most likely to be useful for dating evaporites, salty soil samples (e.g.,

martian soil), and partly weathered rocks. Analysis of salts (in evaporites and soils) and alteration products in igneous rocks may be the most direct means by which to obtain important constraints on the chronology of hypothesized warm, wet epochs on Mars. Analysis of weathered igneous rocks, whether actually desired or not, may be unavoidable if we are to isotopically date volcanic rocks *in situ* on another planet, because it might prove to be very difficult to obtain unweathered material. Stepped dissolution provides a means to obtain information on the age of alteration (or some type of average age if it was a long drawn out process or occurred in multiple episodes) and the original crystallization age if a large amount of the rock's K is still sited in original unaltered remnants of the rock.

Good isochrons obtained by K-Ar analysis with stepped dissolution of terrestrial evaporitic halite from the Permian Palo Duro Basin has shown that this method can yield accurate results for salts that have been undatable by other radiometric techniques (Fig. 3.7; *Wampler and Weaver*, 1987; *Wampler and Hassanipak*, 1986, 1988). Uranium-lead age determinations using slow-stepped dissolution of zircons in concentrated HF acid have recently produced age information of higher quality than the results of the usual single-release method applied to zircons from the same rock (*Mattinson*, 1994). Potassium-argon dating with stepped dissolution seems ideally applicable to the types of rocks and minerals that were formed by precipitation from aqueous solutions, because the laboratory dissolution would provide a crude reversal of the formation processes, unlike methods that achieve decomposition by heating.

However, interpreting remotely measured K-Ar age data will be fraught with uncertainty. If the primary emphasis is placed on knowing the time of igneous activity on planetary bodies, the K-Ar method has been only partly successful. For lunar samples, its greatest successes have been for mare basalts extruded after the large impacts that formed the major basins on the lunar surface, and in dating the times when the basins formed. Potassium-argon dates of prebasin lunar crustal rocks are often influenced by impact-related Ar outgassing, and apparently crustal rocks from Vesta (eucrite meteorites) are also so influenced (*Bogard*, 1995). Finally, the presence of trapped Ar in shergottites has helped to confuse the interpretation of the ages of these meteorites of putative martian origin. If this is true of rocks that petrographically appear to be good igneous basalts, the problems attendant to interpreting the time of formation of martian evaporites and sedimentary rocks must be anticipated. These problems will be exacerbated by the high $^{40}Ar/^{36}Ar$ ratio in the martian atmosphere, which will increase the difficulty of detecting trapped atmospheric Ar when it occurs.

Rubidium-strontium. As discussed above, stepped dissolution has some attractions as a sample extraction method for K-Ar age determinations and could also be useful for Rb-Sr dating. Transfer of dissolved Rb and Sr from solution to ions,

whether by thermal ionization, laser ionization, or whatever, could present problems, but has not been studied in detail. Assuming that transfer is possible, what might we learn by applying Rb-Sr dating to dissolution step fractions?

Consider first the analysis of bulk samples. Assuming that we are able to determine both the isotopic ratio $^{87}Sr/^{86}Sr$ and the elemental ratio $^{87}Rb/^{86}Sr$ to "good" precision, what might we learn, and how good would "good" have to be?

The most unambiguous case would occur for rocks of very low Rb/Sr, as might be seen in plagioclase-rich crust like that of the Moon. If multiple sampling and analyses are possible, such a crust would probably yield individual samples of quite low Rb/Sr. For such a rock, $^{87}Rb/^{86}Sr$ values near BABI would suggest a very ancient crust, while higher values would imply late crust formation and complex petrogenetic processes that produced reservoirs enriched in Rb relative to Sr compared to the bulk planet (e.g., the Earth's crust). To make these inferences, however, $^{87}Sr/^{86}Sr$ values would need to be measured to better than 1%, preferably better than 0.1% (see Table 3.4).

Another favorable case is from samples with Rb/Sr ratios that are much higher than Rb/Sr in the bulk planet, e.g., rocks of granitic composition. These samples would also have high concentrations of K, and thus could be detected from orbit by their high natural radioactivity. Although areas of planetary surfaces with granitic compositions might be quite limited, determining the ages of such areas, in a geological context, could be important for calibrating methods that determine relative age, such as crater count ages.

The ages here are Rb-Sr model ages, calculated from measured $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ of bulk samples, and an assumed value of initial $^{87}Sr/^{86}Sr$ ratio, usually BABI. Among the returned lunar samples, there are some instances in which Rb-Sr model ages are close approximations to igneous ages (Table 3.4). As seen from Table 3.4, comparison between the model and crystallization ages can be rather good if one is willing to accept age uncertainties (errors) of as much as ±20%, with the rationale that an uncertain age is better than no age at all. To achieve this level of uncertainty, $^{87}Sr/^{86}Sr$ must be measured to ~0.1%; for granitic samples, 1% uncertainty would yield reasonable precision on the age. However, this good agreement is to some extent a misleading consequence of the antiquity of all lunar samples, since the "default value" for a Rb-Sr model age is 4.55 Ga. Nevertheless, model ages would imply that the Moon's surface is in general quite "old." The data needed for a model age contains information that can be used for "quality control." That is, when the $^{87}Rb/^{86}Sr$ ratio of a sample is much higher than average, the model age gives a good to excellent approximation to the crystallization age (e.g., granite and KREEP in Table 3.4).

The relatively good agreement between lunar Rb-Sr model ages and crystallization ages cannot be obtained for all planetary samples, for instance the "martian meteorites" (Table 3.5). For the shergottite subgroup of martian meteorites, Rb-Sr model and crystallization ages are distinctly different. This difference could be discounted, however, if the ~180-Ma

TABLE 3.4.   Rb-Sr model ages compared to crystallization ages for lunar surface samples.

Landing Site	Rock Type	Sr (ppm)	$^{87}Rb/^{86}Sr$	ε_{BABI}*	Model Age	Cryst. Age	Error (%)
Apollo 11	Soil	165	0.0461	46.2	4.56		
	Hi-K basalt	165	0.0938	73.1	3.8	3.59	6%
	Lo-K basalt	180	0.0098	9.2	4.52	3.71	22%
Apollo 12	Soil	127	0.144	129.5	4.37		
	Basalt	116	0.0283	16	4.42	3.3	34%
	Granite	114	1.368	1242	4.42	3.99	11%
Apollo 14	Soil	182	0.233	217	4.54		
	KREEP	192	0.1824	164	4.37	3.87	13%
	Granite	64	7.54	6340	4.11	4.13	0
Apollo 15	Soil	130	0.127	119	4.59		
	Basalt	74	0.021	15	4	3.3	21%
	KREEP	187	0.285	249	4.25	3.94	8%
Apollo 16	Soil	170	0.0447	45	4.9		
	Basalt	180	0.0294	26	4.29	3.84	12%
	KREEP	162	0.163	150	4.48	3.93	14%
Apollo 17	Soil	168	0.0256	168	4.84		
	Basalt	181	0.0083	10	5.5	3.82	44%
	KREEP	89	0.0238	210	4.32	4.07	6%

*Enrichment of $^{87}Sr/^{86}Sr$ in ε units (0.01%) relative to lunar initial $^{87}Sr/^{86}Sr = 0.69898$.

"crystallization ages" for the shergottites instead reflect impact melting. It should be noted that the current consensus is that the ~180-Ma ages truly reflect igneous crystallization (*McSween*, 1994). For the rest of the martian meteorites, agreement between model and crystallization ages is much better. In this connection it should be pointed out that martian granites are not represented in Table 3.5. A landing strategy that targeted granitic surface areas as identified from orbit could result in instrument placement in a region where at least some of the local rocks would have Rb-Sr model ages that were good approximations of their crystallization ages. Further, it is reasonable to consider whether ages might also be determined by the K-Ca method. The K-Ca method is completely analogous to the Rb-Sr method, and again works best for high K/Ca materials, e.g., granite. However, K-Ca dating requires much higher precision of measurement than does Rb-Sr dating, so K-Ca is unlikely to be useful for landed surface missions. In the lunar granite with an enhancement

TABLE 3.5.   Rb-Sr model ages compared to crystallization ages for martian meteors.

Meteorite	Rock Type	Sr (ppm)	$^{87}Rb/^{86}Sr$	ε_{BABI}*	Model Age	Cryst. Age	Error
Shergotty	Basalt	51	0.397	352	4.33	0.165	2500%
Zagami	Basalt	43	0.376	335	4.35	0.18	2300%
EET 79001	Basalt	67	0.203	200	4.77	0.178	2600%
ALH 77005	Lherzolite	13	0.172	169	4.77	0.187	2450%
Nakhla	Clinopyroxene	37	0.123	89	3.54	1.31	169%
ALH 84001	Orthopyroxene	4	0.367	360	4.77	4.50	6%

*Enrichment of $^{87}Sr/^{86}Sr$ in ε units (0.01%) relative to lunar initial $^{87}Sr/^{86}Sr = 0.69898$.

of the $^{87}Sr/^{86}Sr$ ratio of 63% (6300 ε units, Table 3.4), the enhancement of the $^{40}Ca/^{44}Ca$ ratio is only 0.5%, or 49ε units.

Uranium-thorium-lead. The U-Th-Pb method of radiometric age determination has received little consideration for use with a landed planetary instrument; the technique as used in terrestrial laboratories employs either extensive chemical preparation of samples or large, high-resolution, ion microprobes with which U-rich phases such as (rare) zircons can be analyzed *in situ*. Recent developments in laser and mass spectrometry technology make it feasible to consider at least the requirements that a laser-based instrument would have to meet in order to yield useful data. The U-Pb data summarized in Table 3.6 for representative extraterrestrial samples are intended to convey the scope of the requirements for such an instrument without being exhaustive in regard to the extraterrestrial sample database.

The U-Pb isotopic system has a well-known advantage relative to other methods of age determination in that model ages can be determined from measurement of the isotopic ratio $^{207}Pb/^{206}Pb$ alone. The utility of the Pb-Pb model ages is limited by the fact that the initial Pb isotopic composition in the sample in question must be known. Thus, Pb-Pb model ages have found greatest applicability among ancient meteorite samples for which it is reasonable to assume that the initial Pb isotopic composition was the same for each sample and equal to the initial value for Pb in the early solar system as determined from laboratory measurements on meteoritic samples with very low U/Pb ratios. Beyond the zeroth order determination of model ages in the range of ~4.55 Ga for primitive meteorites, the Pb-Pb model ages have found application for ordering the formation ages of the meteorites in a fine-scaled chronology. The latter requires a precision of measurement of the $^{207}Pb/^{206}Pb$ ratio of ~0.1%, a value that probably will be difficult to achieve in a remotely operated planetary instrument. However, such a value might be set as a goal for instrument development. A further goal might be to achieve this level of precision for samples of relatively undifferentiated solar system material, represented by the Orgueil carbonaceous (CI) chondrite in Table 3.6.

As an aid to potential instrument developers, Table 3.6 gives typical values of the abundances of ^{238}U, ^{204}Pb, and ^{206}Pb in the samples chosen as representative of different types of "planetary" bodies. Knowledge of the ^{204}Pb abundances in samples is necessary to correct the measured $^{207}Pb/^{206}Pb$ ratios for nonradiogenic initial Pb, required even for the Pb-Pb model ages. Determination of the ^{238}U abundance as well would be very important because it would allow determination of ages using the U-Pb concordia diagram, making the ages so derived much more rigorous. Although Pb isotopic measurements of sufficiently high precision are useful alone for samples of ancient asteroids (and comets?), represented by the first three entries in Table 3.6, useful data for samples of larger planetary bodies such as Mars and the Moon will in general require measurement of U abundances as well. The data in the table imply that precision at least at the percent level for $^{207}Pb/^{206}Pb$ is required for samples in which the ^{206}Pb abundances are at the ~100-ppb level. Samples with very low U and Pb abundances, such as lunar crustal anorthosites, will provide the greatest challenge, whereas once again, granitic samples present the most easily achievable target goals. The Pb-Pb model ages of granitic sample 12013 (or at least the granitic portion thereof) are ~3.9–4.0 Ga, the age generally accepted as the crystallization age of this sample. The lunar granite data represent characteristics of U-Pb data necessary to obtain valid crystallization ages from Pb-Pb ages: high relative abundances of both U and Pb. These characteristics may be met by mineral phases within planetary samples, as well as by rocks on planetary surfaces. An *in situ* analysis capability, as might be provided by a sharply focused laser beam, plus a sample scanning capability, would be highly desirable. A spot size on the order of 30 mm seems a good goal, with better focusing capability desirable, and worse focusing capability up to ~100 mm being useful for analyzing individual mineral grains. If such a capability could be achieved, finding and analyzing a high-U phase would be like "hitting the jackpot," whereas simply analyzing two major mineral phases in a single rock would be a significant augmentation of information compared to a "bulk" analysis of the same rock, provided U abundances could be measured as well as Pb. In the latter case, the possibility would exist for determining an isochron on a concordia diagram, and thus a much more rigorous age measurement than otherwise would be the case. The desirability for such a capability is represented by the data for KREEP "basalt" 14310. (Sample 14310 may actually be an impact melt rock of basaltic composition.) Although the bulk U and Pb data for 14310 appear very similar to those for 12013, the Pb-Pb model age of 14310, ~4.28 Ga, is significantly higher than its 3.88-Ga crystalliza-

TABLE 3.6.   Representative U-Pb data for extraterrestrial samples.

Body	Sample	Type	^{238}U (ppb)	^{204}Pb (ppb)	^{206}Pb (ppb)	Total Pb (ppb)	$^{207}Pb/^{206}Pb$	Refs.
Undiff. asteroids	Orgueil	CI	8	48	450	2434	0.595	[1]
Eucrite parent	Ibitira	Basalt	102	0.15	93	318	0.628	[2]
Angrite parent	ADOR	Magmatic	163	0.24	151	368	0.616	[3]
Mars	Shergotty	Basalt	120	6	88	387	0.921	[4]
Moon	15555	Lo-Ti basalt	144	0.16	98	238	0.405	[5]
	75055	Hi-Ti basalt	157	0.29	137	342	0.577	[5]
	60025	Fer. anorth.	1.8	0.05	2.1	6.7	0.718	[6]
	14310	KREEP	3110	1.65	2475	6122	0.494	[7]
	12013	Granite	5750	3.3	4690	11430	0.534	[8]

References: [1] *Tatsumoto et al.* (1976); [2] *Chen and Wasserburg* (1985); [3] *Wasserburg et al.* (1977); [4] *Chen and Wasserburg* (1993); [5] *Tera and Wasserburg* (1974); [6] *Hanan and Tilton* (1987); [7] *Tera and Wasserburg* (1972); [8] *Tatsumoto* (1970).

tion age. This is because the initial Pb present in this rock had a composition that was significantly more radiogenic than that of "primordial" Pb, used in correcting the measured Pb composition for a nonradiogenic component. Whether or not a ±10% error in age would significantly affect interpretations of planetary evolution based on the age data would depend on the geological context of the sample being analyzed. In any event, analysis of both U and Pb in at least two mineral phases of a sample such as 14310 would be necessary to detect the presence of radiogenic initial Pb.

The above considerations applied to 14310 apply even more forcefully to samples of lower U and Pb concentrations. In particular, this is true of the "martian meteorites." Perhaps because we have no granitic martian meteorites, there are no examples that can be cited for which young Pb-Pb ages can be considered good approximations to the crystallization ages of the samples in question. The Pb-Pb ages of shergottites, for example, are ~4.5 Ga, but the crystallization ages are ~180 Ma. Proper interpretation of the U-Pb data for martian meteorites requires analyses of multiple mineral phases for both U and Pb and interpretation within the framework of the U-Pb concordia diagram.

Cosmic-ray exposure ages. Planetary surfaces exposed to galactic cosmic radiation can be expected to contain products of nuclear reactions as a result of spallation reactions on major elements. This occurs primarily at ~50 cm depth. If the surface material remains undisturbed to this depth, then the age of exposure of the surface can be determined from the production rate of the products. Spallation reactions on a given target element generally produce many different products in roughly equal amounts. In practice, measurements of the three isotopes ^{3}He, ^{21}Ne, and ^{38}Ar, normally the least-common isotopes of the three lightest noble gases, have commonly been used to determine exposure ages. Production rates for these isotopes have been determined from target studies in particle accelerators and nuclear reactors. The production rates, which are dependent on the chemistry and geometry of individual target objects, are typically of the order of 1 atom per gram per minute. The accumulation would then be 10^{-11} g (or, in the terminology used in noble gas studies, 10^{-8} cm^3 STP) per gram per 10^6 yr. Other, "trapped," components for these isotopes must be separated and subtracted from the measured amounts. At ^{3}He and ^{38}Ar, the trapped component sometimes dominates in meteorites and often dominates in lunar samples, leaving ^{21}Ne as the most reliable noble gas isotope for cosmic-ray exposure age determination. Still, precise isotopic measurements, preferably of ^{21}Ne/^{22}Ne and ^{21}Ne/^{20}Ne, are required for separation of the cosmic-ray-produced ^{21}Ne from the trapped component.

The validity of the age depends not only on an accurate measurement of the composition and an accurate assessment of the production rate, but also on the assumption that the material has resided undisturbed within a restricted depth for the period of exposure. The lunar surface presents an example

of a planetary regolith that has been extensively comminuted to depths greater than 1 m for a few billion years. For this reason, "ages" calculated from the total amount of cosmic-ray-produced ^{21}Ne in Apollo regolith samples are regarded with caution and sometimes as meaningless. Only well-documented geologic settings allow for age interpretation (*Walton et al.*, 1973). At the martian surface, accumulation of stable cosmic-ray-produced isotopes in solidified lava flows may indeed be useful for assessing the age of the flows. The challenge would be for remote geologic sampling and accurate (1–5% precision) measurement of quantities necessary for determination of the cosmic-ray contribution to the least abundant isotope of Ne, ^{21}Ne.

The importance of multiple ages and petrographic context. It is not obvious that any of the techniques discussed can actually provide ages meaningful enough to address any of the important questions of planetary evolution and history. Even beyond the analytical difficulties of making the measurements (and few, if any, of the required measurements could be made with the required precision using present technology) and the engineering difficulties of acquiring the right samples, it is often not certain that the "age" obtained is really that of the event of interest. The cosmic-ray exposure ages of the lunar regolith provide one example. The spurious ages of terrestrial salts caused by natural dissolution provide another. The high model U-Pb and Rb-Sr ages of most samples other than granites are yet another. And terrestrial geochronologists are hesitant to accept any age determination based on minerals as poorly characterized as would occur for an *in situ* measurement of U-Pb systematics.

Experience has shown that, in general, radiometric ages can be interpreted with confidence only when concordant ages are measured by two or more techniques, and when interpretation can be made within a known petrographic context. It is still true that by far the best response to these conditions can be made for samples returned to terrestrial laboratories for analysis. If *in situ* analysis is going to be attempted, consideration should be given to the possibility for remote age determinations by more than one method. Finally, if only one method is available, sampling strategies must be considered that maximize the probability of detecting geologically based biases in remotely determined ages.

3.4.2. Improving the Performance of Instruments

A goal for composition analyzer flight instrument development is to approach as closely as possible with *in situ* measurements the analysis precision now possible only with laboratory instrumentation, and to do so with instruments that are compact, low-mass, and reliable.

Measurement precision. For gas analyzers, improvements in traditional techniques (magnetic sector mass analyzers, quadrupole mass analyzers, time-of-flight mass analyzers, ion traps, etc.) are being pursued by a number of groups, and significant advances are possible. The elemental and isotopic

composition of solids is measured through sputtering or ablating surface material into a similar range of types of high-precision mass analyzers. To the extent that future small flight instruments will be able to provide precise isotopic measurements at all masses, they will be important contributors to mission science.

COMPLEX (1994, p. 123) recommended measuring H, C, N, O, and the noble gases in atmospheres to a minimum accuracy of 10%, and the D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, and $^{18}O/^{16}O$ ratios to an accuracy of 1%. These are adequate general guidelines for evolved gases as well as atmospheres, although they might not be sufficient for specific objects. The science questions discussed above for Mars can serve as an example. Viking mass spectrometers measured the abundances and isotopic ratios of the atmospheric constituents on Mars to precisions of 5–50%. The isotopic composition of H and O in water, if known to 1%, would be useful in understanding the current interaction of the atmosphere and surface, and similar benefits would accrue from 1% level C measurements. $^{38}Ar/^{36}Ar$ and $^{129}Xe/^{132}Xe$ ratios would help identify the origin of SNC meteorites as being from Mars, even if measured at 10% levels, but a precision of 1–5% (particularly for $^{38}Ar/^{36}Ar$) would be far better. One of the best tests of the martian origin of SNC meteorites would be from measuring the relative abundances of all three O isotopes, but only if the measurement could be done to a precision of better than 0.1%. Measurement of the $^{20}Ne/^{21}Ne/^{22}Ne$ to a precision of better than 5% would be required to determine cosmic-ray exposure ages. Such measurements (and others such as $^{15}N/^{14}N$, $^{26}Mg/^{25}Mg/^{24}Mg$, etc.) have been made to a much lesser extent for Mars surface materials and for asteroids and comets than they have been for the martian atmosphere. There are many missions in which significant advances can be made with lower-precision isotopic measurements. In addition, comparison of composition over a range of samples (different samples on Mars, different individual comet grains, comet nucleus samples from different depths, diverse asteroid samples, etc.) could show significant and important variations.

Problems encountered in refining the precision of isotopic ratio measurements include overlapping mass numbers of different molecules—mass doublets, e.g., CO and N_2 at 28 dalton, and hydrogenated molecules and the heavier isotope mass number, e.g., ^{12}CH and ^{13}C at 13, or $H_2^{16}O$ and ^{18}O at 18. To overcome this problem, it would be necessary to have mass resolutions of ~3000 to analyze CO (27.9949) and N_2 (28.0061) separately, ~30,000 to analyze ^{40}Ar (39.9624) and ^{40}K (39.9640) separately, and >500 for the hydrocarbons. The Pioneer Venus Large Probe mass spectrometer did have a resolving power of nearly 500. It might be possible to reach 30,000 in future instrumentation (e.g., ion traps, reflectron time-of-flight analyzers, etc.). To the extent that one of the molecules in the mass doublet is produced by fragmentation of a parent molecule during ionization in the instrument, a possible improvement is to use low electron energy to produce the ions without fragmentation. Ionization efficiency de-

creases markedly when the electron energy is less than 25 eV, but with enough gas pressure in the ion source, this method becomes feasible. Selective gettering of one species of a mass doublet may also help alleviate the problem in some cases.

For measurements of solids, techniques such as pulsed laser ablation at relatively high energy density can be used to convert surface compounds into their elemental constituents, avoiding many (but probably not all) of the problems of overlapping molecules and isotopes. This technique is well matched to time-of-flight analysis of the resulting ions.

Dynamic range. There are many factors in an instrument that affect the dynamic range or range of true signals that can be measured. In any mass spectrometer it is not only the full-width (FW) at half-maximum (HM) that determines useful resolution, but the FW at tenth or even hundredth maximum. With broad wings, two mass peaks one atomic mass unit (u) apart will not be resolved if the intensity of one is 10^4, say, that of the other. Isotopic ratios this large are not uncommon (see Fig 3.1).

In a quadrupole mass spectrometer, factors that broaden the wings of a peak are fringing at the quadrupole entrance aperture and large acceptance angle. Some relief is usually gained by using a small aperture relative to the "kissing circle" diameter of the poles, but this results in a loss of signal intensity. Other solutions, such as a tube protruding into the quadrupole region or a field-matching entrance cylinder, are used. In the ion trap, dynamic range is also affected by the sheer ion capacity of the trap. If a miniature trap can only hold 10^3 ions (above which Coulomb collisions cause resolution loss), then frequent fill-sample-dump cycles must be used to measure ion intensities in a ratio of 10^{-4} or less. Duty cycle and efficiency of trapping ions in the well then become important. Larger traps, of course, can hold more ions (order of 10^6) so the problem is less severe. In a Wien filter, beam shear due to the varying energy of the ions across the input ion-beam diameter (caused by the electric field across the plates) smears the output mass spectrum, causing overlapping wings. Small beam diameters are a solution, but signals will again be reduced. In a magnetic sector uniformity of field, magnetic-field fringing at the entrance slit and large input angles will again cause wings.

Occasionally one finds a limit to the dynamic range by a "double-bind" situation. If one is measuring small ion currents on a metal strip, for example, the limit of lower intensities may be electrometer sensitivity or competition from a spurious background (photons, electrons, sputtered or desorbed ions, etc.). The limit of higher intensities (gained by increasing gas pressure or electron-ionizer current) may be ionizer-filament lifetime, detector lifetime, arcing limit of the detector high-voltage, or Paschen breakdown in the ionizer, mass-analyzer, and/or detector.

Instrument miniaturization and compatibility. A corollary to NASA's new mantra of "faster, better, cheaper" is "smaller, lighter, lower power." The future appears to include miniaturization of many types of mass, energy, and velocity

analyzers, without sacrificing important parameters such as mass range, resolution, rejection (spectral wings), dynamic range, and sensitivity. Proper dimensional and voltage scaling must be followed, and the use of many *parallel arrays* of instruments, miniaturized or micromachined, can compensate for the reduced input-aperture area (*Boumsellek et al.*, 1993). Quadrupoles (*Boumsellek et al.*, unpublished data), ion traps (*Hoffman et al.*, unpublished data), and a "mass spectrometer on a chip" (a Wien filter with an extended metal-strip ion collector at the output plane; *Freidhoff et al.*, unpublished data) of dimensions of tens of millimeters have been made to work in several laboratories. A small magnetic sector is also under construction (*Sinha et al.*, unpublished data). Miniaturization (shortening) of time-of-flight or reflectron instruments depends upon fast (subnanosecond) pulsing circuitry and low capacitances and inductances in the flight instrument. Even smaller (0.1–2 mm dimensionality) analyzers are being designed and developed. One approach uses the LIGA method to achieve submillimeter dimensions, retain the often-needed 0.1% dimensional tolerances (amounting to 1 mm in 1000 mm), and provide mass-production capabilities.

In order to "match" system dimensions one must also shrink such items as gas-chromatographic columns, ionizers, detectors, and vacuum pumps. Little work is being done in the last regard, although small turbopumps (7.5 l/s) have recently become commercially available (Alcatel Vaccum Products, Hingham, Massachusetts).

Another less obvious benefit in miniaturization is that the requirement that the particle mean free path be smaller than instrument dimensions implies that shorter mean free paths (higher operating pressures) can be tolerated in the smaller devices. Operating at millitorr or higher pressures means that pumping requirements can be relaxed. However, matching ionizers and detectors must now be capable of emitting and detecting at the higher pressures.

Survivability. An obvious requirement for any instrument to be effective is that it survive long enough to make a sufficient number of measurements. Without meaning to belabor the point, we mention some general problems of survivability, and some problems specific to mass spectrometers and lasers.

General: The extremes of planetary surface temperatures, from a few tens to several hundred degrees Kelvin, will limit the performance and the survival of most electronic instrumentation, including mass spectrometers and lasers. Most "hi-rel" (high reliability) electronic components are designed to survive up to 125°C, but printed circuit cards may become unreliable at that temperature, particularly if they are cycled between extremes, as would happen on a body with no substantial atmosphere. Thermal expansion between the printed wire traces and the boards can cause separation and potential failure.

Dust could also be a hazard in many places, ranging from active comets to the lunar terminator to martian dust storms. Dust is an especially serious hazard for any optical device, such as a laser. Venus might be one of the few places where dust would not be a problem, but its hot, heavy, and corrosive atmosphere has always presented one of the greatest challenges to *in situ* instruments, although several have now been successfully landed.

Mass spectrometers: Gas pressure in the range of 1 torr to 10^{-2} torr can cause problems with high voltages. Corona discharges and acing can occur in this pressure region, the problem being exacerbated with increasing voltage. CO_2 has a lower breakdown voltage than N_2 or O_2, so the problem becomes worse on Mars. It is best to contain high voltages either in a reasonable vacuum ($<10^{-4}$ torr) or near Earth's atmospheric pressure.

Laser extraction systems: The environmental pressure may also influence the performance and survival of lasers. Beams should "zap" targets under near-vacuum conditions to distinguish products from the ambient atmosphere. High environmental pressures would require a pumping system for the extraction chamber and the optical path of the laser. Natural UHV environments, such as the Moon or an asteroid, pose no such problem. Gas lasers, in the vacuum of some planetary surface environments, must have vacuum seals capable of preventing performance- and survival-limiting leaks from occurring.

3.4.3. Sample Selection and Preparation Issues

Gaining answers to many driving scientific questions depends critically on selecting proper samples for analysis and preparing them correctly. Here we give a brief discussion of some of the issues involved. Of course, some questions don't require careful sample selection: To the extent that a body's atmosphere is in equilibrium, atmospheric measurements from any location carry global information. However, evolved gas analyses and, to an even greater extent, age analyses depend critically on sample considerations.

Sample selection. Sample site selection is one of the most crucial aspects of any effort to derive knowledge of a planet's history from its rocks. Each planet or satellite has a unique geology and history, so scientific objectives and site selection criterion will be different for each planetary object. Engineering aspects can seriously constrain target selection, as clearly was the case during the Viking and Mars Pathfinder landing site selection processes. Can the spacecraft deal with a landing on what might be a bouldery volcanic lava flow? Can it reach the poles? Can it survive far from the subsolar latitude? These considerations, in turn, constrain the science that can be done.

If we assume that engineering is not an issue (i.e., one can place a lander where interesting rocks are to be found), the optimum site depends on the scientific objective(s) of the mission. At the lowest level of consideration, this is obvious. For example, if one is interested in obtaining the isotopic age

of a volcanic rock, one normally has to go to a volcanic terrain, whereas if one is interested in obtaining the stable isotopic composition of precipitated ices, the polar caps would be the place to go. Commonly, there are several scientific objectives of a mission and tradeoffs are necessary, since some objectives may be difficult to attain simultaneously. For instance, there are no morphologically fresh unambiguous volcanic deposits in immediate environs of the residual polar ice caps on Mars, so a mission with multiple goals of studying polar ices and volcanic rocks would require considerable mobility.

Furthermore, the site selected must contain rocks that can be used to make the required measurements. Many isotopic studies, particularly radiometric dating studies, require *optimal* sampling, and thus a sampling strategy based on considerable prior knowledge. This sampling strategy may dictate mission strategy and even mission sequencing. All radiometric age determination methods depend on the presence of natural radioactivities. The greater the abundance of the natural radioactivities in a given sample, the easier the task of the geochronologist, and the lower the demands on analytical techniques and equipment. Thus, if the highest-priority scientific goal is to determine the radiometric ages of one or more geologic provinces to absolutely calibrate cratering rates on a given planetary body, for example, then one or more areas having the highest levels of natural radioactivity, but meeting the geological criteria, could be selected on the basis of orbital measurements of γ-ray activity. After landing in an area, there should be some way to select the rocks with the appropriate chemistry (rich in the element of interest) and genesis.

There are additional considerations. For example, a calibration of the cratering rate curve through geologic time on any planet would be difficult with only a single sample. At best, it would be possible to determine one point on the curve (although if that point were judiciously selected it could still be scientifically quite significant). Similarly, the experience analyzing Apollo cores showed that variations in volatile contents in a single core are dominated by local stratigraphy, and the same may be true of cores of polar deposits. Determining isotopic shifts from weathering interactions (e.g., on Mars or Venus) or transport processes (polar volatile deposits of Mercury and perhaps the Moon) is a less daunting task than determining ages. However, it still requires fairly precise measurements and careful selection of rock samples that might show the desired effect.

In some cases it might be possible to gain both global and local information from a single site, if it is possible to find exposed bedrock and globally distributed soil at the same site. This might be especially useful if the ubiquitous martian dust consists of minerals that were formed by hydrogeologic activity and then redistributed by eolian processes that would not disturb isotopic signatures. Similarly, samples of regoliths on small asteroids may be something approaching global, but for some problems (such as surface exposure dating) analyses would be most useful if accompanied by analysis of bedrock.

Sample preparation. Sample preparation will have to be a consideration for any analysis of gas extracted from solids (i.e., evolved gas), no matter what technique is used. For example, in the lunar regolith, volatiles are concentrated in a thin (>1 mm) shell at the outer edges of grains, and hence might be susceptible to loss by abrasion. Thus, any experiment on lunar volatiles would have to be careful to neither destroy nor contaminate the surfaces of grains. Weathering products on Venus or Mars, or volatiles in the regolith of an asteroid, would also be expected to be concentrated near surfaces.

One of the key advantages terrestrial chronology studies have over robotic *in situ* measurements is the terrestrial analyst's ability to select subsamples by their mineralogy. One might conceive of a robotic mechanism scheme to perform mineral separations *in situ*, or at least to grind or crush a sample until a vision system could detect mineral enhancements. But the price of such a scheme would be not only complexity, but also weight and hence expense; thus it seems unlikely that any processing-intensive technique will be worth considering. Simpler strategies, such a tools to chip or dust off samples to expose a fresh surface, are more likely to be feasible.

3.5. SUMMARY

3.5.1. Atmospheric Composition

Mass spectrometers have successfully analyzed several atmospheres, but, as is usually the case in science, have generated as many questions as they have answered. To make further progress, mass analyzers need to be more precise than their predecessors. The *COMPLEX* (1994) goal of 10% precision for the all the noble gases, H, C, O, and N, and 1% precision for the isotopes of H, C, N, and O, is a reasonable target. In addition, these higher-performance mass analyzers need to be miniaturized to a level that will fit on the smaller spacecraft to be expected in coming years.

3.5.2. Evolved Gases

Some version of evolved gas analysis, usually involving some volatile element, is a priority at virtually every conceivable target. Little has been done with evolved gases to date, so it seems almost inevitable that any successful measurement will produce interesting science. Analysis of elements or compounds may not need to be of high precision to be useful. However, since the isotopic shifts expected are often much smaller than the difference between atmospheres, it seems prudent to try to detect isotopic ratios with at least the precision recommended for future atmospheric studies.

3.5.3. Ages

Several working groups have identified the determination of radiometric ages as among the highest-priority objectives. To determine ages to 10% precision (sufficient to answer

current questions for every body except the Moon) would require an uncertainty of less than 10% of the expected shift in the isotopic ratio being measured. From Tables 3.4, 3.5, and 3.6, it can be seen that while 1% measurement precision will suffice in a few cases, precision of 0.1% or better is more commonly needed. If there is an underlying assumption that radiometric ages will be determined remotely on a representative sampling of a given landing site, we consider such aspirations unrealistic. If, however, the goal is one of determining one or a few ages on an optimal sampling of material, we believe the odds of success improve dramatically. Several possible radiometric (and cosmic-ray-based) techniques have been discussed above. A solicitation of interest may well turn up other candidates, after which a funding program could be developed to pursue two or three of the most promising ideas. The alternative, which in many cases demands less extrapolation of technology, is to use *in situ* missions for characterization, and attempt to develop inexpensive sample return missions for detailed chronologic studies.

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